SHORT PAPER

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Synthesis and reaction of a chiral cluster containing an SRuNiW core[†]

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The new cluster [NiRuW(CO)$_5$(μ_3-S)(η^5–C$_5$H$_5$)(η^5–C$_5$H$_4$COCH$_3$)] **2** was isolated from the reaction of [CoRuW(CO)$_8$(μ_3-S) (η^5–C$_5$H$_4$COCH$_3$)] **1** with NiCp$_2$. Through the further reaction of cluster **2** with 2,4-dinitrophenylhydrazine, a new cluster [NiRuW(CO)$_5$(μ_3-S)(η^5–C$_5$H$_5$)(η^5–C$_5$H$_4$C(NNH-C$_6$H$_3$-2,4-(NO$_2$)$_2$)CH$_3$)] **3** was obtained and the structure of cluster **2** has been established using single crystal X-ray diffraction method.

Keywords: chiral cluster, SruNiW core

Hetero-metal cluster complexes have been attracting intense attention since the mid-70s,[1–3] especially in recent years the structural and bonding aspects of mixed-metal tetrahedral skeleton clusters have been extensively studied.[4–5] One important reason is that such chiral clusters can induce an asymmetric catalysis potentially.[6] In our research group, considerable efforts have been directed to the synthesis of chiral tetrahedral clusters containing four different atoms or groups at the vertices of a tetrahedron. Recently we have described the synthesis and structure of chiral clusters containing the core MruCoS.[7–8] In this paper, we would like to describe the synthesis (shown in Scheme 1) and structure of novel chiral clusters [NiRuW(CO)$_5$(μ_3-S)(η^5 –C$_5$H$_5$)(η^5 –C$_5$H$_4$COCH$_3$) **2** and [NiRuW(CO)$_5$(μ_3-S)(η^5 –C$_5$H$_5$)(η^5 –C$_5$H$_4$C(NNH-C$_6$H$_3$-2,4-(NO$_2$)$_2$)CH$_3$)] **3** containing the SRuNiW core. Both **2** and **3** are air-stable crystals and soluble in polar solvents. Satisfactory C, H analyses were obtained for the two compounds.

The spectra of **2** and **3** show intense terminal carbonyl absorption bands in the range 2069-1929 cm^{-1}, characteristic of CO ligands bounding to transition metals, together with one additional absorption band at 1663 cm^{-1} for the C=O carbonyl in cluster **2** and one band at 1616 cm^{-1} for the C=N double bond in cluster **3**. The ^{1}H NMR spectra of **2** and **3** show one single peak at δ 5.42ppm and δ 5.34ppm, respectively, assigned to the protons on the cyclopentadienyl ring attached to the Ni atom. In addition, the ^{1}H spectrum of **2** and **3** exhibit four asymmetric singlets in the range δ 6.01–5.53 for the cyclopentadienyl protons attached to the Mo atom.

The crystal structure of **2** was determined by X-ray crystal structure analysis. As shown in Fig. 1, the structure of cluster **2** contains a tetrahedral framework comprised of S, Ru, Ni and Mo atoms. Five carbonyls and two cyclopentadienyl ligands are coordinated to the three transition metals. In cluster **2** all

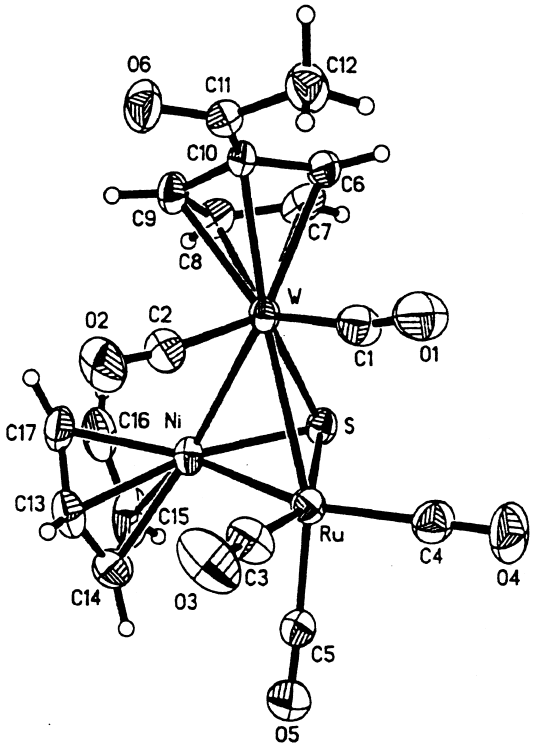
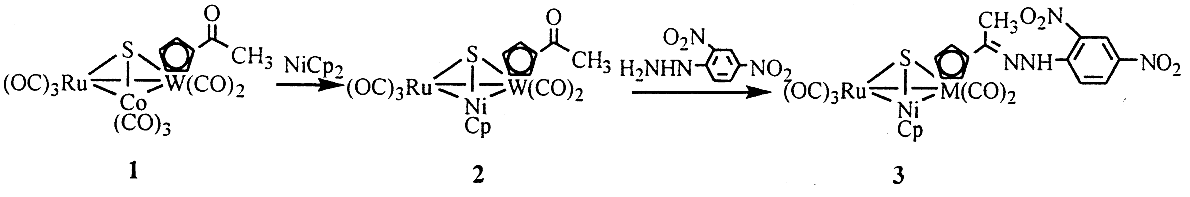


Fig.1 Crystal structure of the cluster **2**.
Selected bond distances (Å) and angles (°): W–S 2.3768(16), W–Ni 2.6380(9), W–Ru 2.8414(6), Ru–S 2.3224(17), Ru–Ni 2.5673(10), Ni–S 2.1419(18), S–W–Ni 50.24(4), S–Ni–Ru 58.26(5), S–W–Ru 51.93(4), S–Ni–W 58.54(5), Ni–W–Ru 55.73(2), Ru–Ni–W 66.15(2), S–Ru–W 53.68(4), Ni–S–Ru 70.08(5), Ni–Ru–W 58.12(2), Ni–S–W 71.22(5), S–Ru–Ni 51.66(5), Ru–S–W 74.40(5).



Scheme 1

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

the C atoms in the substituted cyclopentadienyl together with C(11), C(12) and O(6) in the $COCH_3$ group, are located in one plane. This the π-system of the substituted group $COCH_3$ is fully conjugated with the cyclopentadienyl π-system. This result is in contrasted to that reported by Song *et al*.[9]

Finally it is important to note that while the three carbonyls attached to the Ru atom are terminal in the two molecular structures, there is a semi-bridging carbonyl (one carbonyl bound to W atom C1) in the fragment $Mo(CO)_2(C_5H_4COCH_3)$. The asymmetry parameter α (0.405) is well within the range for semi-bridging carbonyls.[10] The coexistence of both terminal carbonyls and semi-bridging carbonyls is consistent with the IR spectra of **2** showing an absorption band at 1870 cm^{-1}.

Experiment

All reactions were carried out under pure nitrogen using standard Schlenk techniques. All solvents were dried and deoxygenated according to standard procedures before use. Chromatographic separations and purification were performed on 160–200 mesh silicon gel. Infrared spectra were recorded as pressed KBr disks on a Nicolet FT-IR 10 DX spectrometer. ^1H NMR spectra were recorded on a Bruker AM-400 MHz spectrometer in $CDCl_3$-deurated solvent at ambient temperature. Elemental analyses were performed on an 1106-type analyzer. $NiCp_2$,[11] $[CoRuW(CO)_8(\mu_3\text{-}S)(\eta^5\text{–}C_5H_4COCH_3)]$[7] **1** were prepared according to literature methods.

Preparation of cluster **2**: The cluster **1** (250mg, 0.35mmol) and $NiCp_2$ (110 mg, 0.58mmol) were dissolved in THF (25ml). After the mixture was refluxed for 17 h, the solvent was removed under reduce pressure and the residue was extracted with CH_2Cl_2 (5ml). Then the extracts were subjected to column chromatography separation using 1:10 CH_2Cl_2/petroleum ether as eluent. Several small bands with a major one were developed. From the main black band was obtained 60 mg (25.0%) of **2** as a purple solid. Calcd for $C_{17}H_{12}O_6WNiRuS$: C, 29.68; H, 1.76. Found: C, 29.70; H, 1.75. IR (KBr disk): 2069vs, 2008s, 1987vs, 1929s, 1870s (CO); 1663s (C=O). $\delta_H(CDCl_3)$: 5.99-5.61 (m, 4H, C_5H_4), 5.42 (s, 5H, C_5H_5), 2.37 (s, 3H, CH_3).

Preparation of cluster **3**: 2,4-Dinitrophenylhydrazine solution (1.0 ml), prepared by dissolving 2,4-dinitrophenylhydrazine (500 mg) in 98% H_2SO_4 (2.5 ml), H_2O (5 ml) and ethanol (17.5 ml), was added to an ethanol solution (15 ml) in which cluster **2** (35 mg, 0.050mmol) was dissolved. After the mixture was reacted at room temperature for 1 h, the solvent was removed under reduce pressure and the residue was extracted with CH_2Cl_2 (5ml). Then the extracts were subjected to silica gel column chromatography separation using 1:1 CH_2Cl_2/petroleum ether as eluent. Several small bands with a major brown one were developed. From the main brown band was obtained 30 mg (68.2%) of **3** as a brown solid. Calcd for $C_{23}H_{16}O_9N_4WNiRuS$: C, 31.82; H, 1.86; N, 6.45. Found: C, 31.79; H, 1.88; N, 6.46. IR(KBr disk): 3111w (N-H), 2053vs, 1978vs, 1930m, 1861m(CO), 1616s (C=N), and 1592s (NO_2) cm^{-1}. $\delta_H(CDCl_3)$: 11.20 (s, 1H, N-H), 9.09 (s, 1H, H^3 of benzene ring), 8.32–8.29 (d, 1H, H^5 of benzene ring, *J*=9.88 Hz), 7.90–7.87 (d, 1H, H^6 of benzene ring, *J*=9.08), 6.01–5.53 (q, 4H, C_5H_4), 5.34 (s, 5H, C_5H_5), 2.16 (s, 3H, CH_3).

Crystal Data for **2**: Crystal **2** ($C_{17}H_{12}O_6WNiRuS$, Mr=687.96) used for the X-ray structure determination were obtained from hexane-CH_2Cl_2(1:1) solution at –20 °C. The space group was $P\bar{1}$. The crystals were mounted on a glass fibre. Preliminary examination and data collection were performed with Mo–Kα (λ=0.71073 Å) radiation on a CCD area detector equipped with graphite monochromator: *a*=7.9267(4), *b*=8.5850(5), *c*=14.7024(8) Å. b=104.9610(10), Z=2, V=939.82(9) Å^3, Dc=2.431 g/cm^3, μ=8.031mm^{-1}, $2q_{max}$=56.50° and F(000)=648. The final cycle of full-matrix least-squares refined was based on 4173 observed reflections [I>2.00σ(I)] and 246 variable parameters and converged at final R=0.0514, R_w= 0.1313. Minimum and maximum final electron densities were –4.306 and 4.615 eÅ^{-3}. The structures were solved by direct method using the SHELXS-97 program. The non-hydrogen atoms were refined anisotropically. Hydrogen positions were calculated by geometrical methods.

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